

Experimental investigation of NO_x emissions in oxycoal combustion

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ABSTRACT

This work presents the results of an experimental investigation on NO_x emissions from coal combustion in a pilot scale test facility. Three oxidiser atmospheres have been compared, namely air, CO₂/O₂, and O₂ enriched recirculated flue gas. NO_x emissions from two different combustion modes have been studied, swirl flame and flameless combustion. The influence of the burner oxygen ratio and the oxidiser O₂ concentration on NO_x formation and reduction have been analysed. With increasing burner oxygen ratio, an increase of NO_x emissions has been obtained for air and CO₂/O₂ in both, swirl flame and flameless combustion. In case of the swirl flame, flue gas recirculation leads to a reduction of NO_x emissions up to 50%, whereas in case of flameless combustion this reduction is around 40% compared to CO₂/O₂. No significant impact of the oxidiser O₂ concentration in the CO₂/O₂ mixture on NO_x emissions is observed in the range between 18 and 27 vol.% in swirl flames. An analysis of NO_x formation and reduction mechanisms showed, that the observed reduction of NO_x emissions by flue gas recirculation cannot be attributed to the reduction of recirculated NO_x alone, but also to a reduced conversion of fuel-N to NO.

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1. Introduction

Combustion of fossil fuels results in the formation of oxides of nitrogen (NO_x), either by fixation of atmospheric nitrogen (via the thermal or prompt NO mechanisms for NO formation), or by conversion of nitrogen containing structures in the fuel (the fuel NO mechanism). Due to the relatively high content of nitrogen in coal and its extensive use as fuel, coal combustion is a major source of anthropogenic NO_x emissions, and mechanisms for formation of NO_x from combustion of coal have been extensively studied. Combustion of coal under controlled conditions has demonstrated that NO production via the fuel NO mechanism dominates under the regime of temperatures and residence times found in full-scale pulverised fuel fired furnaces [1,2]. There are two opposing factors that influence fuel NO_x emissions during coal combustion: (i) the oxidation of fuel-N by oxygen and other oxidising agents, and (ii) the reduction of already produced NO_x by reducing agents, such as hydrocarbons from pyrolysis of the volatile matter (homogeneous reactions) and resident char (heterogeneous reactions).

Numerous technologies are available nowadays to control NO_x formation and reduction inside pulverised fuel fired furnaces. These methods, known as primary measures, differ significantly in cost, effectiveness, complexity, and extent of modifications required to achieve a reduction of NO_x emissions. A combination of those is commonly used to comply with regulatory emission limits.

With oxyfuel combustion, that is burning of fuel in a mixture of oxygen and recycled flue gases, see also [3–5], NO_x emissions from pulverised fuel boilers are significantly reduced. Compared to air-fired units, NO_x emissions generated per energy released during oxyfuel combustion are around 60–70% lower depending on the burner design, coal type and operating conditions [5–10]. Moreover, according to Normann et al. [9], conventional primary control measures should be sufficient to reduce NO_x emissions in oxyfuel firing to meet equivalent regulatory limits. This substantial NO_x decrease is presumed to be the result of the two following mechanisms [11,12]. Firstly, thermal NO formation is reduced due to the absence of atmospheric N₂. Secondly, recycled NO is reduced to form molecular nitrogen after being supplied through the flame: (i) by CH fragments from the pyrolysis of volatile matter; (ii) by interaction between recycled NO and released fuel N, mainly HCN and NH₃, and (iii) catalytically on the char surface. According to Mendiara and Glarborg [13], an increase of the CO₂ concentration affects the ratio of the concentrations of radicals (O/H/OH), thus leading to an increased probability of formation of N₂ from NH₃ instead of NO.

Park et al. [14] studied the fuel-N conversion during heterogeneous reaction of bituminous coal char with O₂, CO₂ and H₂O over a broad range of temperatures, pressures and reactant gas concentrations. The results showed that char-N is converted entirely into N₂ when char reacts with CO₂; into N₂ and NO when char reacts with O₂; and into HCN, NH₃ and N₂ when char reacts with H₂O. Previous simulations of a combustion system with high in-furnace recirculation rates [15] showed that the recirculation causes in-

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creased char oxidation by CO_2 and H_2O . Together these two studies show that the amount of char-N released as N_2 is rather independent of the recycling ratio as long as the flue gas is not dried, since the increased N_2 release due to oxidation by CO_2 is compensated by the increased release of intermediate species by oxidation with H_2O . Supposedly, char-N to NO conversion can thus be influenced by drying of the recycled flue gas and thereby adjusting its vapour content. Moreover, Cao et al. [16] showed that a high concentration of nitrogen intermediates in the combustion zone, which can be achieved by wet recycling, is favourable for NO reduction.

Next to conventional reduction techniques, Liu and Okazaki [17] as well as Normann et al. [9] proposed an increase of the combustion temperature as a means to facilitate NO_x reduction via the thermal path.

The conversion of fuel-N to NO_x increases with the O_2 concentration in the oxidiser [18–20]. However, Shaddix and Molina [19] showed that this effect is less pronounced or even reversed at O_2 concentrations below 24 vol.%. According to Hu et al. [12] and Liu and Okazaki [17], the NO reduction efficiency increases with equivalence ratio and recycling ratio. As the recycling ratio increases, the heterogeneous reaction between NO and char is promoted in the early stages of coal combustion by high CO concentrations, which are obtained as a result of the low O_2 content in the inlet gas. However, the resulting decrease of fuel concentration has an inverse effect on the reduction of NO_x because of the decrease in hydrocarbon fragment concentrations. Hence, there is a contrary effect of O_2 content on the emission of fuel NO and the reduction of recycled NO_x .

This paper focuses on NO_x emissions as function of the burner oxygen ratio defined according to the following equation:

$$\text{oxygen ratio} = \lambda = \frac{m_{\text{O}_2}/m_{\text{fuel}}}{(m_{\text{O}_2}/m_{\text{fuel}})_{\text{stoichiometric}}}$$

and furthermore on NO_x emissions as function of the O_2 content in the oxidiser. The oxygen concentration has been varied between 18 and 27 vol.% in the oxidiser as the required oxygen concentration depends on the process topology of the oxyfuel power plant [3,21]. Three different combustion atmospheres were considered, namely, air, CO_2/O_2 , and O_2 enriched recycled flue gas. Furthermore, experiments have been carried out with a swirl burner which has been optimised for oxyfuel combustion as well as with a burner for flameless combustion. The motivation for this work is to investigate in more detail the processes of NO_x formation and reduction in oxy-combustion of pulverised coal at oxygen concentrations similar to those in air. Moreover, the differences in NO_x emissions from combustion in air, CO_2/O_2 and a flue gas recycle mode are evaluated.

2. Experimental setup

2.1. Test facility

Experiments were conducted in a vertical, cylindrical, top fired furnace with an inner diameter of 400 mm and a total length of 4200 mm, Fig. 1. In the centre of the furnace, 2100 mm from the top, four ports give access to the combustion chamber for optical and probe measurements. The burner is axially traversable allowing for measurements at different distances from the burner through a single measurement plane. Alternatively, the measurement ports can also be used for the injection of staging air when the burner is traversed to higher positions. Moreover, the test facility is equipped with an electric heating system with which the wall temperature can be regulated. A schematic of the furnace with peripheral equipment is given in Fig. 2.

The test facility can be operated in three different modes: air, dry oxyfuel and wet oxyfuel. Air and dry oxyfuel refer to

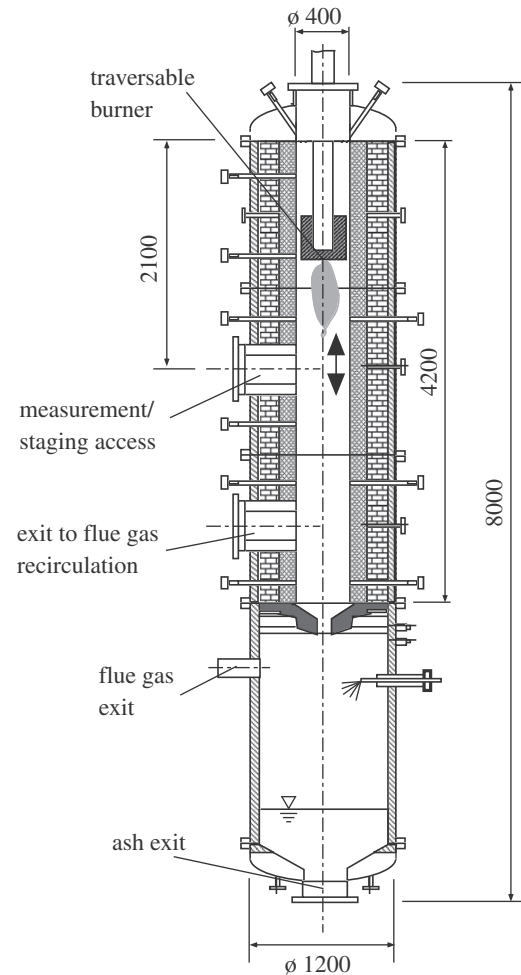


Fig. 1. Furnace geometry, all dimensions in [mm].

once-through-modes with air (point 12 in Fig. 2) or respectively a mixture of CO_2 and O_2 as oxidiser (point 7). Wet oxyfuel refers to a flue gas recycling (FGR) mode, where a part of the flue gas is recycled and enriched with oxygen up to a concentration of 21 vol.%. First of all, fly ash is removed in the recirculation (point 2), then the flue gas is enriched with oxygen (point 3), cooled to a manageable fan inlet temperature by a flue gas cooler (point 4) and fed to a reservoir (point 6) by a flue gas fan (point 5). The oxygen concentration in the oxidiser stream in dry oxyfuel mode has been varied between 18 and 27 vol.% and in wet oxyfuel between 18 and 21 vol.%.

In air mode, coal is either carried by air (with a reduced oxygen content of 19 vol.% due to inertisation of the coal feeding system – point 8 in Fig. 2) or by nitrogen. In dry oxyfuel mode, the oxygen concentration in the coal carrier is limited to a maximum of 21 vol.% in a mixture of O_2 and CO_2 . As an alternative, pure CO_2 can also be used as coal carrier. In wet oxyfuel mode, coal is carried by a mixture of CO_2 and O_2 with 19 vol.% O_2 .

2.2. Burners

Two different burners have been used in this investigation: one swirl burner and one burner for flameless combustion. The burner geometries and dimensions are shown in Fig. 3.

The swirl burner is a scaled up version of the burner presented in detail by Toporov et al. [22]. It has an annular orifice through which the coal and carrier stream are injected. The part of the

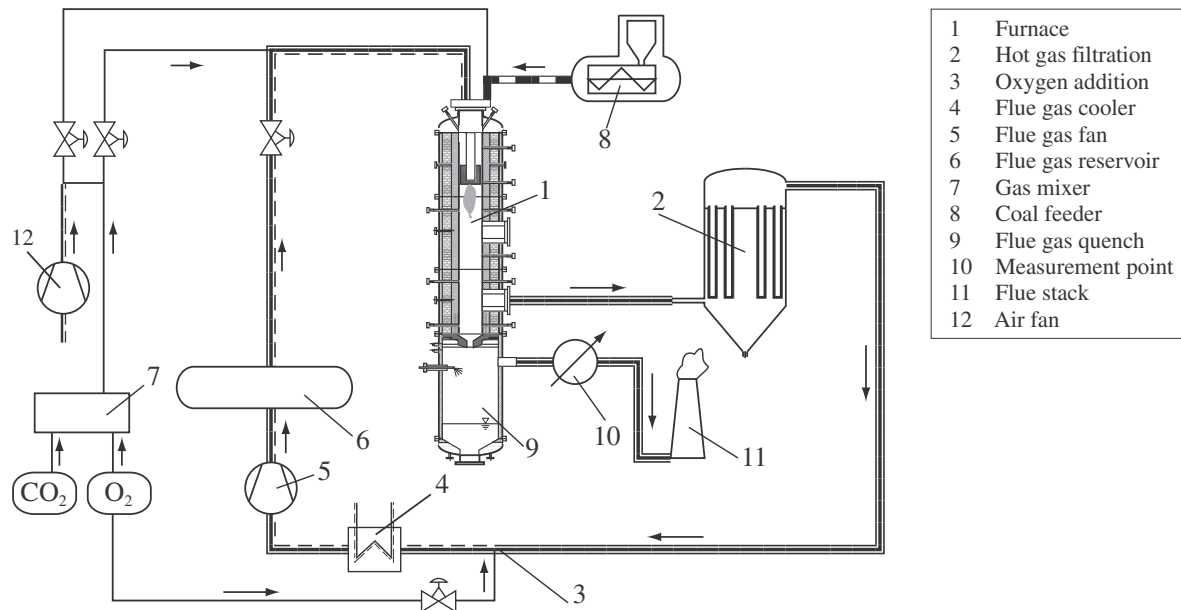


Fig. 2. Schematic of the test facility.

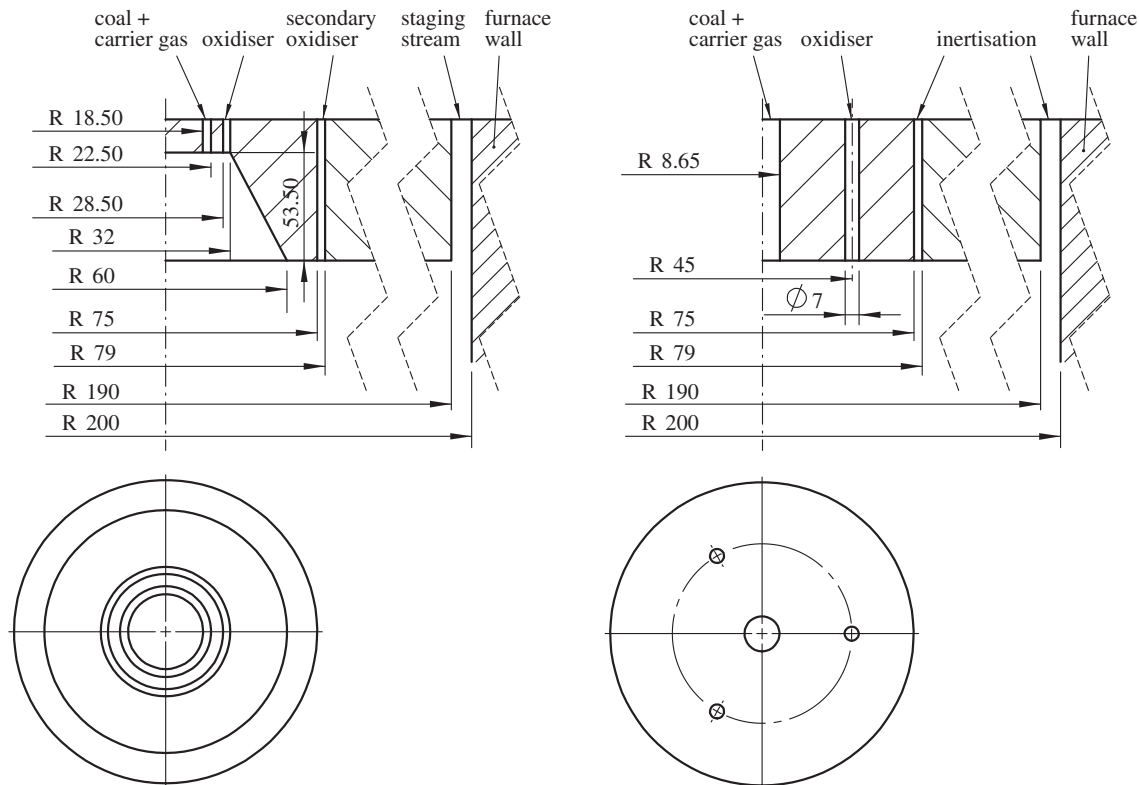


Fig. 3. Burner design of swirl burner (left side) and flameless combustion burner (right side), sectional view on top and bottom view below.

oxidiser which is injected through the burner throat enters through an annulus surrounding the coal inlet. It can be swirled whereas the swirl number (ratio of tangential to axial momentum) has been set to ≈ 0.9 for all experiments within this test campaign. The burner throat opens with an half-angle of 28° . A secondary oxidiser stream is injected through an annulus enclosing the burner throat. Another gas stream, the staging fluid, enters the furnace

through an annulus at the outer diameter of the furnace. Its main purpose is to reduce the amount of gas which is injected through the burner thus reducing the velocity and the local stoichiometry at the burner. The flow field achieved with this burner type has been described in detail by Toporov et al. [22]. In wet oxyfuel mode, only the swirled oxidiser stream and the staging stream at the outer wall of the furnace are recycled, hence only a fraction

Table 1

Operational parameters for swirl and flameless combustion.

Mode	λ_b	O ₂ concentration		Thermal input (kW)	Volume flows (stp)				RR
		Oxidiser (vol.%)	Coal carrier (vol.%)		Carrier (m ³ /h)	Oxidiser (m ³ /h)	Sec. oxidiser (m ³ /h)	Staging stream (m ³ /h)	
Swirl burner									
Air	0.42–0.77	21	19	100–54	9.4	24.5	3.0	72–21	0.59–0.58
Dry	0.57–1.05	21	19	74–40	9.4	24.5	3.0	43–6	
Wet	0.60–0.57	21	19	74–70	9.4	24.5	3.0	43–39	
Dry	0.6	18–27	16–21	47–87	9.4–8.2	24.5	3.0	39–37	
Dry	0.6	20–25	0	52–65	9.4	24.5	3.0	30	0.58–0.60
Wet	0.6	18–21	19	60–70	9.4	24.5	3.0	39	
					Volume flows (stp)				
					Carrier (m ³ /h)	Oxidiser (m ³ /h)	Inner/outer inert. (m ³ /h)	Staging stream (m ³ /h)	
Flameless combustion									
Air	0.6–1.1	21	0	41–22	9.4	22.9	2.5 / 6.0	27–4	0.19–0.34
Dry	0.6–1.1	21	0	41–22	9.4	22.9	2.5 / 6.0	27–4	
Wet	0.6–1.1	21	0	41–22	9.4	22.9	2.5 / 6.0	27–4	

of around 60% of the flue gas is recycled. The recycling ratio (RR) is defined as the ratio between the mass of flue gas being recycled and the total flue gas mass flow.

$$RR = \frac{\text{recycled flue gas}}{\text{total flue gas}}$$

Experiments with the swirl burner have been carried out with the burner traversed to a position close to the measurement plane so that the overall furnace length from the burner level to the furnace exit was reduced to 2200 mm.

The flameless combustion burner has a central circular inlet through which the coal is injected. It is surrounded by three equally spaced circular inlets on a circumference with a diameter of 90 mm through which the oxidiser is injected. A small purge flow of N₂ in air mode and respectively CO₂ in either oxyfuel mode was injected through the two outer annuli mentioned above. The flow field achieved with this burner type has been described in detail by Ristic et al. [23]. For flameless combustion experiments, the burner has been traversed to a position 1200 mm above the measurement plane giving a total furnace length of 3300 mm. Necessary staging air was injected via the measurement ports so that experiments have been carried out with a length of the primary combustion zone of 1200 mm.

In wet oxyfuel mode with the flameless combustion burner, the oxidiser stream is the only recycled stream resulting in a fraction between 19 and 34 vol.% of the flue gas being recycled depending on the burner oxygen ratio (λ_b). Based on the total gas streams in the primary combustion zone (oxidiser, coal carrier, and inertisation), a fraction of 56 vol.% comes from the FGR.

2.3. Operational parameters

In order to investigate the influence of the burner oxygen ratio λ_b and the operation mode on NO_x emissions, comparative experiments have been carried out with both burners. The operational parameters for these experiments are summarised in Table 1.

The burner oxygen ratio was varied in a range of $0.42 \leq \lambda_b \leq 1.05$ for the swirl burner and $0.6 \leq \lambda_b \leq 1.1$ for the flameless burner. Furthermore, the oxygen concentration in the oxidiser has also been varied in the range from 18 to 27 vol.% for the swirl burner.

To eliminate aerodynamic effects, the gas streams supplied at the burner (coal carrier, oxidiser and secondary oxidiser stream as well as the inner inertisation) were kept at a constant volume

flow throughout all measurements with a burner. To allow for a variation of the burner oxygen ratio λ_b while keeping aerodynamic conditions constant, the coal mass flow and thus the thermal load had to be adjusted. While the burner oxygen ratio was altered (Fig. 4), the thermal load of the swirl burner varied from 54 to 100 kW_{th} in air, from 40 to 74 kW_{th} in dry oxyfuel and from 70 to 74 kW_{th} in wet oxyfuel mode. During the variation of the oxygen concentration in the oxidiser (Figs. 6 and 7), the thermal load in wet oxyfuel mode ranged from 60 to 70 kW_{th}, while in dry oxyfuel mode it varied from 47 to 87 kW_{th} with O₂/CO₂ as coal carrier and from 52 to 65 kW_{th} with CO₂ as coal carrier stream. For the flameless combustion burner the thermal load ranged from 22 to 41 kW_{th} (Fig. 5).

The staging stream was adapted accordingly to retain the overall oxygen ratio and to compensate for changes of the oxidiser oxygen concentration. Therefore, a lower burner oxygen ratio (given an unchanged oxygen content) results in a higher coal mass flow and a bigger staging stream, while a lower oxygen content (with $\lambda_b = \text{const}$) decreases the coal mass flow and leaves the volume flow of the staging stream constant.

The overall oxygen ratio for the swirl and the flameless burner was set constant at $\lambda = 1.2$ and $\lambda = 1.3$, respectively. This setting leads to approximately the same final O₂ concentration due to the higher fraction of inert streams in the flameless combustion mode. However, due to uncertainties in the coal mass flow and some residual O₂ in the inertisation streams (about 1% O₂ in N₂)

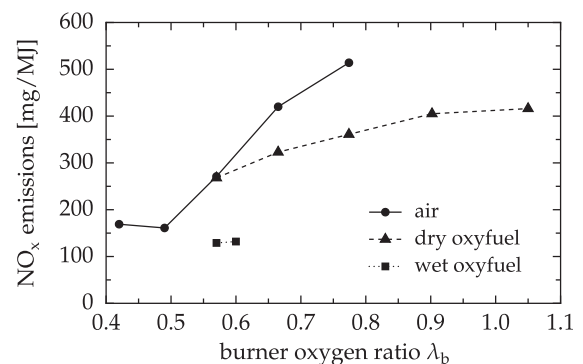


Fig. 4. NO_x emissions over burner oxygen ratio with swirl burner under different operation modes (oxygen concentration in oxidiser 21 vol.% for all operation modes).

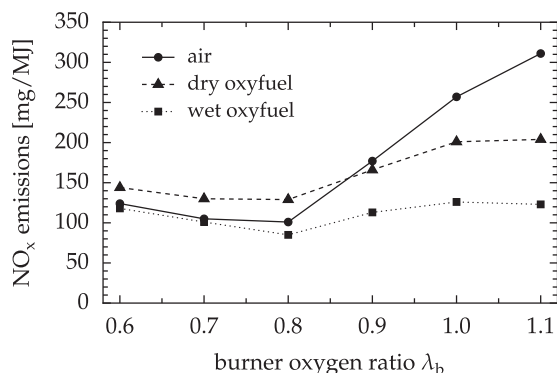


Fig. 5. NO_x emissions over burner oxygen ratio with flameless combustion burner under different operation modes (oxygen concentration in oxidiser 21 vol.% for all operation modes).

the actual burner oxygen ratio in both cases is in the range of $1.3 < \lambda < 1.4$.

When using the swirl burner, the staging stream was inserted through the outer annular opening. During operation with the flameless burner the secondary oxidiser and the outer annular opening were purged with an inert gas stream (N₂ in air mode and CO₂ in either oxyfuel mode) of 2.5 and 6 m³/h (at STP), respectively.

The wall temperature was kept within a range between 900 and 1000 °C. In-flame measurements of the temperature distribution for similar burners have been previously published by Toporov et al. [22] (swirl burner) and Ristic et al. [23] (flameless burner). The composition of the coal (Rhenish lignite) is given in Table 2. The coal is ground to a particle size distribution of $d_{90} < 48 \mu\text{m}$ and $d_{50} < 17 \mu\text{m}$.

The NO concentration is measured by means of NDUV (Non Dispersive Ultraviolet Spectrography) in dry flue gas in the stack as indicated in Fig. 2 (point 10). The measurement range is from 0 to 1000 ppm with a maximum relative error of 0.5% of the upper limit. For comparison of emissions from the individual operation modes, the NO concentration in the flue gas has been converted to emissions based on the thermal input. For this, NO is considered as NO₂.

3. Results

3.1. Influence of burner oxygen ratio λ_b on NO_x emissions

The following figures present data from global NO_x emission measurements. Fig. 4 shows a comparison of NO_x emissions from the three different operation modes with the swirl burner. In air mode, NO_x emissions with this burner are significantly higher than emissions obtained with state of the art low NO_x burners. The reason for this behaviour is twofold. Firstly, the walls of the test facility are heated in order to obtain an adiabatic furnace so that NO_x emissions cannot be simply compared to an industrial application. Secondly, the burner has been optimised for oxyfuel combustion

by inducing a strong inner recirculation of hot flue gas which is necessary to ignite the reactants under oxyfuel conditions. This causes high temperatures in the burner vicinity and thus favours the formation of thermal NO.

At a burner oxygen ratio of $\lambda_b \approx 0.6$, NO_x emissions are around 265 mg/MJ for both, air and dry oxyfuel mode. For higher burner oxygen ratios the increase in NO_x emissions in dry oxyfuel mode is slower than in air mode so that NO_x emissions for $0.65 < \lambda_b < 0.8$ in dry oxyfuel are about 25–30% lower than in air.

For the wet oxyfuel mode, NO_x emission data is only available for a burner oxygen ratio of $\lambda_b \approx 0.6$. Here, NO_x emissions are at around 130 mg/MJ. Thus, compared to the dry oxyfuel mode, NO_x emissions are reduced by approximately 50%.

Fig. 5 presents equivalent data obtained with the flameless combustion burner described above. NO_x emissions are roughly halved compared to the swirl burner at all investigated burner oxygen ratios for air and dry oxyfuel mode. Up to a burner oxygen ratio of $\lambda_b = 0.8$, NO_x emissions are in the same range between 100 and 150 mg/MJ in all three operation modes. At $\lambda_b > 0.9$ NO_x emissions in air mode exceed those in dry oxyfuel mode by 25–50 %. Below $\lambda_b \leq 0.9$, NO_x emissions in air mode are similar to or even below those in dry oxyfuel mode.

In flameless combustion mode, the FGR does not significantly reduce NO_x emissions up to a burner oxygen ratio of $\lambda_b = 0.8$. However, the recycle ratio (RR) is only about 19% at $\lambda_b = 0.6$ and rises to 34% at $\lambda_b = 1.1$. For burner oxygen ratios $\lambda_b \leq 0.8$, NO_x emissions from flameless combustion show a minor increase with decreasing burner oxygen ratio for all operation modes. NO_x emissions in wet oxyfuel combustion stay in the range between 100 and 150 mg/MJ throughout all burner oxygen ratios. This corresponds to a NO_x reduction of 40% in the recycle mode compared to the once through mode for $\lambda_b > 0.9$.

Table 3 shows NO_x concentrations in the FGR after addition of oxygen. The trend is similar to the trend shown in Fig. 5 and exhibits a minimum at a burner oxygen ratio of $\lambda_b = 0.8$ in both the volumetric concentration of NO and NO₂ as well as the mass of NO_x based on the thermal input. The NO₂ concentration is in the order of 5% of the total NO_x which is similar to the fraction in conventional pulverised coal firing systems. In addition, the total mass of NO_x at the end of the furnace (prior to the split-up between the stack and the FGR) and the recycle ratio (RR) are given in the last two columns, too. Together with the emission data reported in Fig. 5 these data indicate that no NO is formed or reduced within the FGR.

3.2. Influence of oxidiser O₂ concentration on NO_x emissions

One important design parameter in oxyfuel combustion is the O₂ concentration in the oxidiser. The burner has to operate with an oxygen concentration which is determined from the desired temperature and heat transfer in the furnace. Thus, a further inves-

Table 2
Proximate and ultimate analysis in [m.%] of predried Rhenish lignite.

Proximate analysis		Ultimate analysis (daf)	
Water	9.59	C	69.31
Ash	8.86	H	5.12
Volatiles	42.85	O	24.21
Char	38.70	N	1.07
LHV	22.3 MJ	S	0.29

Table 3
Nitrogen oxide concentration in the FGR for flameless combustion (oxygen ratio $\lambda = 1.3$).

Burner oxygen ratio λ _b	Oxidiser			Furnace end NO _x (mg/MJ)	RR
	NO (ppm)	NO ₂ (ppm)	NO _x (mg/MJ)		
0.6	95	6	32	146	0.19
0.7	77	4	30	132	0.23
0.8	61	3	27	115	0.26
0.9	81	4	40	160	0.29
1.0	93	6	52	184	0.32
1.1	89	6	55	187	0.34

tigation of NO_x emissions with respect to the O_2 concentration in the oxidiser has been carried out. Fig. 6 presents data from the swirl burner. Dry oxyfuel combustion is compared to wet oxyfuel combustion whereby for dry oxyfuel combustion the O_2 concentration in the coal carrier has been varied, too (see Table 1). However, no difference can be seen between CO_2 and a mixture of CO_2 and O_2 as coal carrier. For dry oxyfuel combustion at an oxygen concentration of 18 vol.%, NO_x emissions are in the order of 300 mg/MJ. With increasing O_2 content, there is a slight trend to reduced NO_x emissions down to 200 mg/MJ at 27 vol.% which is consistent with previously published data [22]. However, at oxidiser oxygen concentrations of 18–20 vol.% as well as at 27 vol.%, the CO concentration in the flue gas was in the range of 200–300 ppm which could have caused reduced NO_x emissions to some extent, whereas it was below 100 ppm for all other measurements. The overall conversion of fuel N to NO_x is in the order of 15–30%. In wet oxyfuel combustion, NO_x emissions are between 50 and 120 mg/MJ between an O_2 concentration of 18 and 21 vol.%.

Table 4 shows NO_x concentrations in the FGR after addition of oxygen for the swirl burner. Here, the fraction of NO_2 is below 4% of total NO_x . Again, the increase of the NO_x concentration in the FGR is proportional to the increase in the furnace. Thus, no NO is produced or reduced within the FGR.

Fig. 7 presents equivalent data on CO emissions for the measurements conducted with varying O_2 concentrations. As a reference, CO emissions during combustion in air are below 30 mg/MJ for all measurements. In particular, at a burner oxygen ratio of $\lambda_b = 0.57$ – comparable to data presented in Fig. 7 – CO emissions were 28 mg/MJ. Thus, CO emissions are similar in air and in dry oxyfuel mode. CO emissions in wet oxyfuel mode are significantly lower at about 3–10 mg/MJ for all oxidiser oxygen concentrations whereas in dry oxyfuel mode CO emissions increase towards 170 mg/MJ at an oxidiser oxygen concentration of 18 vol.%.

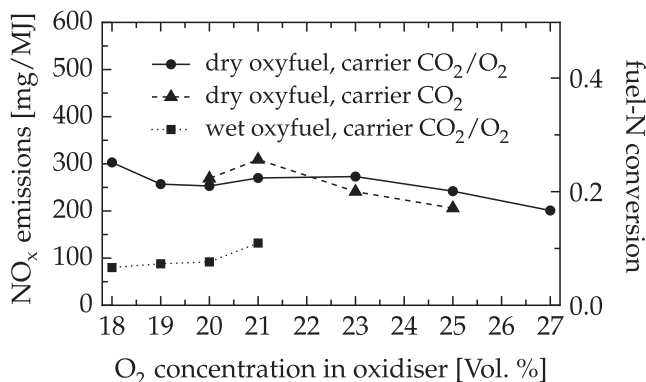


Fig. 6. NO_x emissions over oxidiser oxygen concentration (swirl burner at a burner oxygen ratio of 0.6).

Table 4

Nitrogen oxide concentration in the FGR for swirl burner (oxygen ratio $\lambda = 1.2$, burner oxygen ratio $\lambda_b \approx 0.6$, recycle ratio $RR \approx 0.6$).

O_2 conc. in oxidiser (vol.%)	Oxidiser			Furnace end NO_x (mg/MJ)
	NO (ppm)	NO_2 (ppm)	NO_x (mg/MJ)	
18	180	0	108	201
19	203	2	117	215
20	221	3	121	223
21	324	9	173	315
21	337	11	179	314

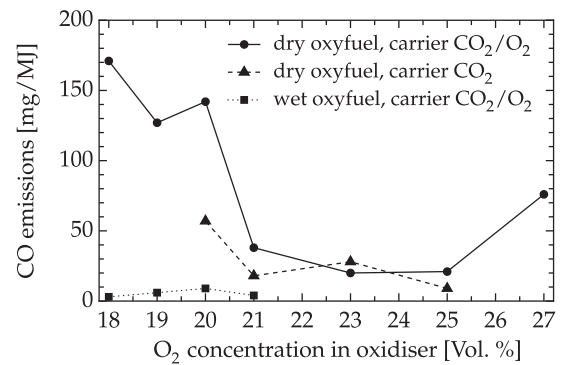


Fig. 7. CO emission over oxidiser oxygen concentration (swirl burner at a burner oxygen ratio of 0.6).

4. Discussion

The general trend to increased NO_x emissions with increased burner oxygen ratio in oxyfuel combustion shown by Kiga et al. [24] for an oxidiser oxygen concentration of 30 vol.% can be confirmed with the current experiments for an oxygen concentration of 21 vol.%. This effect is more pronounced in the swirl flame but can also be observed in flameless combustion for burner oxygen ratios larger than $\lambda_b \geq 0.8$. The slight increase of the NO_x emissions for decreasing burner oxygen ratios below $\lambda_b = 0.8$ can be explained by an increase in fuel NO as discussed below.

4.1. Thermal NO

For the swirl flame the fraction of NO_x emissions that is produced via the thermal NO path can be estimated to 25–30% by evaluating the difference between air and dry oxyfuel mode in Fig. 4. Due to the absence of atmospheric nitrogen in oxyfuel firing, all NO that is produced in this operation mode can be considered fuel NO. However, since the increased CO_2 concentration influences combustion progress and since the flame temperature in oxyfuel operation differs from that in air due to the higher molar heat capacity of CO_2 , the actual amount of fuel-N to NO conversion probably also differs between air and oxyfuel operation so that the difference between NO_x emissions in air and in dry oxyfuel combustion only gives a rough estimation of thermal NO.

The fraction considered thermal NO is slightly higher compared to data from standard swirl burners [25,26]. The burner is designed to induce a strong inner recirculation of hot reaction products to the burner mouth in order to stabilise the flame in oxyfuel mode. This intense recirculation causes the increased formation of thermal NO in air mode. At burner oxygen ratios below $\lambda_b = 0.6$, no thermal NO seems to be produced. This can be attributed to the reduction of the oxygen concentration in the burner proximity at low burner oxygen ratios.

The trend for flameless combustion shown in Fig. 5 differs from that for the swirl burner in Fig. 4. Earlier experiments of flameless combustion in an atmosphere of O_2 and Ar [2] indicated about 40% thermal NO at a burner oxygen ratio of $\lambda_b = 0.8$. In the current investigation, thermal NO formation is prevented almost completely up to a burner oxygen ratio of $\lambda_b = 0.9$. Moreover, experiments carried out in air show slightly reduced NO_x emissions compared to experiments in dry oxyfuel mode for $0.6 \leq \lambda_b \leq 0.8$. This trend indicates an increase in fuel NO production in dry oxyfuel mode.

With respect to oxidiser O_2 concentration NO_x emissions with the swirl burner follow the same trend as experimental data published earlier [2,22]. For the dry oxyfuel mode, NO_x emissions can

be considered constant or slightly decreasing with increasing oxidiser oxygen concentration. This is contrary to the trend found for the wet recycle mode and to investigations at higher oxidiser oxygen concentrations by Croiset and Thambimuthu [6], Williams et al. [27], as well as Hjærtstam et al. [28] who showed an increase of NO_x emissions with increasing O_2 content in the oxidiser. However, following the argumentation by Liu and Okazaki [17] and Normann [9], this stagnation or decrease of NO_x emissions could be interpreted as an indicator of improved thermal NO reduction caused by an increase of the adiabatic flame temperature with increasing O_2 content in the oxidiser.

4.2. Fuel NO

Several mechanisms affect fuel NO emissions under oxyfuel conditions, partly in opposite directions. Fuel-N conversion under oxyfuel conditions is reduced compared to the air mode which is to some extent due to a reduced oxidation of HCN as reported by Giménez-López et al. [29].

However, the experiments indicated an increase in fuel NO production in dry oxyfuel mode, especially for flameless combustion (see the difference between NO_x emissions in air mode and dry oxyfuel mode at low burner air ratios in Fig. 5). This can be explained by higher char NO emissions which could partly compensate for the reduced oxidation of HCN. This effect was already reported by Spinti and Pershing [30] who found a slightly negative dependence of char-N to NO conversion with respect to flame temperature.

Moreover, a high concentration of CO_2 enhances the formation of NO under reducing conditions while it inhibits NO formation under stoichiometric and lean conditions as has been reported by Mendiara and Glarborg [13]. This finding could give another explanation for the trend of slightly increased NO_x emissions with reduced oxidiser oxygen concentration shown in Fig. 6.

4.3. NO_x reduction

The reburning effect due to the FGR is much more pronounced with the swirl burner than in flameless combustion mode. Supposedly, at the low level of NO_x concentration in flameless combustion, the reduction mechanisms for recycled NO_x are not as efficient anymore. Moreover, flameless combustion is characterised by a strong recirculation within the furnace itself so that the impact of the flue gas recycle is reduced. However, as mentioned above, as the burner oxygen ratio increases, the recycle ratio also increases which correlates to higher NO_x reduction rates (difference between dry oxyfuel and wet oxyfuel) at higher burner oxygen ratios. This effect has already been shown by Hu et al. [31] who also showed, that the reduction efficiency of recycled NO_x is improved with increasing recycle ratio. Here, the concurring effects of increasing NO_x emissions with increasing burner oxygen ratio and improved NO_x reduction by increasing recycle ratio are combined giving an overall almost constant trend of NO_x emissions in wet oxyfuel mode. On the contrary, Dhungel et al. [32] reported no significant difference in dependence of NO_x emissions on burner oxygen ratio between air mode and an oxyfuel mode with 27 vol.% O_2 in the oxidiser.

Commonly, the main cause for the reduction of NO_x emissions in oxyfuel combustion compared to air is attributed to homogeneous reduction of recycled NO_x , see for example Okazaki and Ando [11]. However, especially from Tables 3 and 4 it becomes obvious, that a reduction of all recycled NO_x would not be sufficient to explain the low NO_x emissions in wet oxyfuel mode compared to dry oxyfuel mode. Thus, next to a high reduction ratio of recycled NO_x the fuel-N conversion ratio is also reduced in wet oxyfuel as compared to dry oxyfuel. The biggest differ-

ence between the two modes is the increased concentration of water vapour in wet oxyfuel due to the recirculation of the combustion products (between 13% and 14% with the swirl burner and around 6% in flameless combustion). Apparently, H_2O inhibits the oxidation of intermediates to form NO or the NO reduction with the intermediates is substantially improved. Schäfer and Bonn [33] have shown, that the addition of water vapour significantly enhances the hydrolysis of HCN to NH_3 . Another effect that reduces NO_x emissions in either oxyfuel mode is, that due to the increase of the CO_2 concentration, the CO concentration also increases which enhances char catalysed reduction of NO_x as was reported by Okazaki and Ando [11].

While the reduced fuel-N conversion in wet oxyfuel mode is not so pronounced in flameless combustion, its effect is largest at low oxygen concentration experiments with the swirl burner. At an oxidiser oxygen concentration of 18 vol.% the reduction of the fuel-N conversion ratio is more than 30% compared to dry oxyfuel mode whereas NO_x emissions at an oxidiser oxygen concentration of 21 vol.% could as well be explained without a reduction of the fuel-N conversion ratio. An increased oxygen concentration could compensate the positive effect of the increased water concentration. One possible explanation is the improved oxidation of intermediate species due to the higher oxygen concentration and a second explanation is the increased temperature at higher oxygen concentrations which enhances NO_x formation.

5. Conclusions

An experimental investigation on NO_x emissions from coal combustion has been carried out. The study showed, that with increasing burner oxygen ratio an increase of NO_x emissions has been obtained for air and dry oxyfuel in both, swirl flame and flameless combustion. In air, the increase in NO_x emissions in case of the swirl flame is higher than in dry oxyfuel mode for $\lambda_b \geq 0.6$ due to the onset of thermal NO formation whereas in case of flameless combustion the onset of thermal NO formation is shifted to $\lambda_b \geq 0.9$.

Flue gas recirculation leads to a reduction of NO_x emissions of up to 50% for the swirl flame, whereas in flameless combustion this reduction is around 40% compared to CO_2/O_2 .

Increasing the O_2 concentration in the range between 18 and 27 vol.% in swirl flames causes a slight reduction of NO_x emissions in dry oxyfuel. However, if a trend is assumed in the data for wet oxyfuel, this trend seems to be reversed compared to dry oxyfuel. Nevertheless, in wet oxyfuel NO_x emissions remain much lower compared to dry oxyfuel in the investigated range of O_2 concentrations (18–21 vol.%).

Assuming that all NO_x that is recirculated is reduced in the flame is not sufficient to explain the obtained low emissions of NO_x . Thus, the conversion of fuel-N to NO in the recycle mode seems to be reduced compared to dry oxyfuel. Apparently, water vapour inhibits the oxidation of intermediates to form NO.

This work demonstrates that wet recycling is preferable in terms of NO_x emissions. However, further investigations on the influence of water vapour on NO_x mechanisms during oxyfuel coal combustion are needed.

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References

- [1] Pershing D, Wendt J. Pulverized coal combustion: the influence of flame temperature and coal composition on thermal and fuel NO_x . In: 16th Symposium (international) on combustion; 1977. p. 389–99.
- [2] Stadler H, Ristic D, Förster M, Schuster A, Kneer R, Scheffknecht G. NO_x -emissions from flameless coal combustion in air, Ar/O_2 and CO_2/O_2 . *Proc Combust Inst* 2009;32:3131–8.
- [3] Buhre B, Elliott L, Sheng C, Gupta R, Wall T. Oxy-fuel combustion technology for coal-fired power generation. *Prog Energy Combust Sci* 2005;31:283–307.
- [4] Wall TF. Combustion processes for carbon capture. *Proc Combust Inst* 2007;31:31–47.
- [5] Wall T, Liu Y, Spero C, Elliott L, Khare S, Rathnam R, et al. An overview on oxyfuel coal combustion-state of the art research and technology development. *Chem Eng Res Des* 2009;87/8:1003–16.
- [6] Croiset E, Thambimuthu K. NO_x and SO_2 emissions from O_2/CO_2 recycle coal combustion. *Fuel* 2001;80:2117–21.
- [7] Nozaki T, Takano S, Kiga T, Omata K, Kimura N. Analysis of the flame formed during oxidation of pulverized coal by an O_2 - CO_2 mixture. *Energy* 1997;22(2/3):199–205.
- [8] Tan Y, Croiset E, Douglas MA, Thambimuthu KV. Combustion characteristics of coal in a mixture of oxygen and recycled flue gas. *Fuel* 2006;85:507–12.
- [9] Normann F, Andersson K, Leckner B, Johnsson F. Emission control of nitrogen oxides in the oxy-fuel process. *Prog Energy Combust Sci* 2009;35:385–97.
- [10] Liu H, Zailani R, Gibbs B. Pulverized coal combustion in air and in O_2/CO_2 mixtures with NO_x recycle. *Fuel* 2005;84:2109–15.
- [11] Okazaki K, Ando T. NO_x -reduction mechanism in coal combustion with recycled CO_2 . *Energy* 1997;22:207–15.
- [12] Hu Y, Kobayashi N, Hasatani M. Effects of coal properties on recycle- NO_x reduction in coal combustion with O_2 /recycled flue gas. *Energy Convers Manage* 2003;44:2331–40.
- [13] Mendiara T, Glarborg P. Ammonia chemistry in oxy-fuel combustion of methane. *Combust Flame* 2009;156:1937–49.
- [14] Park D-C, Day SJ, Nelson PF. Nitrogen release during reaction of coal char with O_2 , CO_2 and H_2O . *Proc Combust Inst* 2005;30:2169–75.
- [15] Stadler H, Toporov D, Förster M, Kneer R. On the influence of the char gasification reactions on NO formation in flameless coal combustion. *Combust Flame* 2009;156(9):1755–63.
- [16] Cao H, Sun S, Liu Y, Wall TF. Computational fluid dynamics modeling of NO_x reduction mechanism in oxy-fuel combustion. *Energy Fuels* 2010;24:131–5.
- [17] Liu H, Okazaki K. Simultaneous easy CO_2 recovery and drastic reduction of SO_x and NO_x in O_2/CO_2 coal combustion with heat recirculation. *Fuel* 2003;82:1427–36.
- [18] Croiset E, Thambimuthu K, Palmer A. Coal combustion in O_2/CO_2 mixtures compared with air. *Can J Chem Eng* 2000;78/2:402–7.
- [19] Shaddix CR, Molina A. Nox formation in laboratory investigations of oxy-coal combustion. In: Fall meeting of the Western states section of the Combustion Institute, No. 07F-43. CA, USA: Livermore; 2007.
- [20] Liu H, Zailani R, Gibbs B. Comparisons of pulverized coal combustion in air and in mixtures of O_2/CO_2 . *Fuel* 2005;84:833–40.
- [21] Stadler H, Beggel F, Habermehl M, Persigehl B, Kneer R, Modigell M, et al. Oxyfuel coal combustion by efficient integration of oxygen transport membranes. *Int J Greenhouse Gas Control*. doi:10.1016/j.ijggc.2010.03.004.
- [22] Toporov D, Bocian P, Heil P, Kellermann A, Stadler H, Tschunko S, et al. Detailed investigation of a pulverized fuel swirl flame in CO_2/O_2 atmosphere. *Combust Flame* 2008;155:605–18.
- [23] Ristic D, Schuster A, Santamaria J, Plion P, Hesselmann G, Wünnig JG, et al. Development of a pilot-scale flameless oxidation burner for ultra low NO_x combustion of pulverised coal. Final Report RFC-PR-04016, Research Fund for Coal and Steel. ISBN: 978-92-79-14226-0 (2010). doi:10.2777/80339.
- [24] Kiga T, Takano S, Kimura N, Omata K, Okawa M, Mori T, et al. Characteristics of PC combustion in the system of oxygen/recycled flue gas combustion. *Energy Convers Manage* 1997;38:129–34.
- [25] Pershing D, Wendt J. Relative contributions of volatile nitrogen and char nitrogen to NO_x emissions from pulverized coal flames. *Ind Eng Chem Process Des* 1979;18(1):60–7.
- [26] Hill SC, Smoot LD. Modeling of nitrogen oxides formation and destruction in combustion systems. *Prog Energy Combust Sci* 2000;26:417–58.
- [27] Williams TC, Shaddix CR, Schefer RW. Effect of syngas composition and CO_2 -diluted oxygen on performance of a premixed swirl-stabilized combustor. *Combust Sci Technol* 2008;180:64–88.
- [28] Hjartstam S, Andersson K, Johnsson F, Leckner B. Combustion characteristics of lignite-fired oxy-fuel flames. *Fuel* 2009;88(11):2216–24.
- [29] Giménez-López J, Millera A, Bilbao R, Alzueta M. HCN oxidation in an O_2/CO_2 atmosphere: an experimental and kinetic modeling study. *Combust Flame* 2010;157:267–76.
- [30] Spinti JP, Pershing DW. The fate of char-N at pulverized coal conditions. *Combust Flame* 2003;135:299–313.
- [31] Hu Y, Kobayashi N, Hasatani M. The reduction of recycled- NO_x in coal combustion with O_2 /recycled flue gas under low recycling ratio. *Fuel* 2001;80:1851–5.
- [32] Dhungel B, Mönckert P, Maier J, Scheffknecht G. Investigation of oxy-coal combustion in semi-technical test facilities. In: Third international conference on clean coal technologies for our future, Cagliari, Italy; 2007.
- [33] Schäfer S, Bonn B. Hydrolysis of HCN as an important step in nitrogen oxide formation in fluidised combustion. Part 1. Homogeneous reactions. *Fuel* 2000;79:1239–46.